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FOKKER-PLANCK EQUATIONS FOR DESORPTION

by

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled FOKKER-PLANCK EQUATIONS FOR DESORPTION submitted by David Bruce Jack in partial fulfillment of the requirements for the degree of Master of Science.

ABSTRACT

After reviewing some of the previous work concerning kinetic equations for desorption a comparison is made between the Kramers-Fokker-Planck equation, derived from classical mechanics, and a Fokker-Planck type equation (GKTT equation) recently developed by Gortel, Kreuzer et al, from a quantum statistical theory of phonon-mediated desorption. To facilitate the comparison both equations are expressed in terms of scaled action-angle variables. It is found that by ignoring terms of the order of the thermal fluctuations in the GKTT equation, it reduces to the low friction case of Kramers' equation. The friction coefficient is identified and when expressed in terms of the microscopic parameters is identical, up to a multiplicative constant, to the expression obtained classically by Caroli et al.

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

I. INTRODUCTION

A gas particle is said to physisorb onto the surface of a solid if the net interaction between the gas particle and the solid, accounted for by an effective wall or surface potential $V_s(\vec{r})$, localizes the gas particle near the solid surface. The surface potential typically consists of a long-range attractive tail, which is essentially the interaction energy between the mutually induced fluctuating dipole moments on the adsorbing gas particle as well as in the solid, and, a short-range repulsive core which is largely due to increasing charge density fluctuations as the adsorbing particle becomes confined close to the surface. Those gas particles trapped into the bound states of the surface potential constitute the adsorbate. Typical binding energies for physisorption, as measured by the heat of adsorption Q, are less than or even much less than 1 eV; e.g. for Xe-W, $Q = 0.402$ eV and for He-C, $Q = 0.012$ eV.

Physisorption is one end of a range of adsorption phenomena of which the other extreme is chemisorption. For the latter the adsorbed molecule undergoes a chemical change by, for instance, forming bonding orbitals with the solid. For chemisorption, Q is typically a few electron-volts. In this thesis we shall deal only with physisorption.

Theories of physisorption fall into two categories; equilibrium and nonequilibrium. Whereas equilibrium theories attempt to calculate quantities such as the adsorption isotherm, specific heats, isosteric heat of adsorption etc., nonequilibrium theories address themselves to the kinetics of the adsorption and desorption processes. The first such kinetic theory was developed at a phenomenological level by Langmuir in 1918[1]. The first quantum mechanical theory was put forward by Lennard-Jones, Devonshire and Strachan around 1935[2]. They argued that the desorbing gas particle acquires the energy necessary to leave the potential trap through its coupling to the phonon bath of the solid. This point of view has been successfully exploited in the recent quantum mechanical theory of Gortel, Kreuzer et al[3,4], where second order perturbation theory was used to calculate the phonon-mediated desorption rates. The potentials considered in the above theory developed, at most, only a few bound states.

Potentials with a large number of states and classical theories have also been put forward. For gas-solid systems at low coverage one argues that a stochastic description based on a master equation is sufficient. Such master equations for desorption kinetics have been constructed for classical models by, e.g. Pagni[5], Pagni and Keck[6], Müller and Brenig[7], etc. A theory based on quantum statistical mechanics has recently been developed by

Kreuzer et al[8,9,10]. Once confronted with a master equation one typically works at deriving a simpler partial differential equation of the Fokker-Planck type. This has indeed been done by the latter authors, thus making a connection to the pioneering work done by Kramers in 1940[11].

Although the papers by Kreuzer et al derive a Fokker-Planck type equation, which they use to study desorption kinetics, an explicit comparison with Kramers' work was not given. This is the task of this thesis. In chapter II we will briefly review the Kramers theory and later developments, and give an outline of the quantum statistical theory of Kreuzer et al. To facilitate an explicit comparison of these two theories, we will, in section III.1-3, cast both in terms of action-angle variables. In this form the quantum statistical theory becomes somewhat more transparent, allowing a justification of some of the earlier approximations, and indeed to go beyond them. To our great surprise we found that, in the low friction limit, the microscopic expression for the friction coefficient in the Kramers-Fokker-Planck equation, as derived from the quantum statistical theory, is identical, up to a multiplicative constant, with that obtained from a classical theory by Caroli et al [12]. This is explained by the fact that low friction results from weak coupling in the gas-solid system and hence many one-phonon processes must occur before a particle can desorb, a situation that can also be described by classical mechanics.

II. REVIEW OF PREVIOUS WORK ON KINETIC EQUATIONS FOR DESORPTION

II.1 Classical Theories

In 1940 Kramers developed a theory of a particle trapped in a potential well out of which it can escape through the action of its Brownian motion[11]. Intended as a microscopic theory of chemical reactions it has found application in the problem of gas particles desorbing from a solid surface. Kramers' theory, which we want to briefly outline in this section, requires the construction of a Fokker-Planck type equation for the particle distribution function in phase space.

We start with the Kramers-Langevin equation[13],

$$\frac{dp}{dt} = F(r) - \eta p + \mathcal{F}(t) \quad , \tag{2.1}$$

where $p = m\dot{r}$ is the momentum of the particle of mass m trapped in the potential, r its coordinate, $F(r) = -\frac{\partial U(r)}{\partial r}$ is the force exerted on the particle by the potential, and the friction coefficient η is related to the random force $\mathcal{F}(t)$ by,

$$\eta = \frac{1}{mk_B T} \int_0^\infty <\mathcal{F}(0)\mathcal{F}(t)> dt \tag{2.2}$$

with

$$< \mathcal{F}(0)\mathcal{F}(t) > = C\delta(t) \quad , \tag{2.3}$$

being the time correlation function for the stochastic variable $\mathcal{F}(t)$. From this stochastic equation an equivalent

Fokker-Planck equation may be derived for the probability density $n(r,p,t)$. If the particle undergoes a random walk in phase space, then

$$n(r,p,t) = \int g(r,p,t;r',p',t')\,n(r',p',t')\,dr'\,dp' \;, \tag{2.4}$$

where the propagator $g(r,p,t;r',p',t')$ satisfies the Smoluchowski-Chapman-Kolmogorov equation

$$g(r,p,t;r',p',t') = \int g(r,p,t;r'',p'',t'')\,g(r'',p'',t'';r',p',t')\cdot \cdot dr''\,dp'' \;. \tag{2.5}$$

To derive a second order partial differential equation we follow Kac and Logan[14] and define jump moments for small time increments $\Delta t = t-t''$:

$$\int (r-r'')\,g(r,p,t;r'',p'',t-\Delta t)\,dr\,dp = \langle (r-r'')\rangle_{\Delta t} \sim A_r(r'',p'')\,\Delta t, \tag{2.6a}$$

$$\int (p-p'')\,g(r,p,t;r'',p'',t-\Delta t)\,dr\,dp = \langle (p-p'')\rangle_{\Delta t} \sim A_p(r'',p'')\,\Delta t, \tag{2.6b}$$

$$\int (r-r'')(p-p'')\,g(r,p,t;r'',p'',t-\Delta t)\,dr\,dp = \langle (r-r'')(p-p'')\rangle_{\Delta t} \sim B_{rp}(r'',p'')\,\Delta t \;, \tag{2.6c}$$

$$\int (p-p'')^2\,g(r,p,t;r'',p'',t-\Delta t)\,dr\,dp = \langle (p-p'')^2\rangle \sim B_{pp}(r'',p'')\,\Delta t \;, \tag{2.6d}$$

$$\int (r-r'')^2\,g(r,p,t;r'',p'',t-\Delta t)\,dr\,dp = \langle (r-r'')^2\rangle \sim B_{rr}(r'',p'')\,\Delta t \;. \tag{2.6e}$$

Now, multiply (2.5) by a well-behaved test function, $\phi(r,p)$, and integrate over variables r and p to obtain,

$$\int g(r,p,t;r',p',t)\,\phi(r,p)\,dr\,dp = \iint g(r,p,t;r'',p'',t'')\,\cdot$$

$$\cdot\ g(r'',p'',t'';r',p',t')\,\phi(r,p)\,dr''\,dp''\,dr\,dp\ . \qquad (2.7)$$

Expanding $\phi(r,p)$ in a Taylor series about (r'',p''),

$$\phi(r,p) = \phi(r'',p'') + (r-r'')\frac{\partial\phi}{\partial r} + (p-p'')\frac{\partial\phi}{\partial p}\Bigg|_{\substack{r=r''\\ p=p''}} + \frac{1}{2!}(r-r'')^2\frac{\partial^2\phi}{\partial p\partial p}\Bigg|_{\substack{r=r''\\ p=p''}}$$

$$+ (r-r'')(p-p'')\frac{\partial^2\phi}{\partial r\partial p}\Bigg|_{\substack{r=r''\\ p=p''}} + \frac{1}{2!}(p-p'')^2\frac{\partial^2\phi}{\partial p\partial p}\Bigg|_{\substack{r=r''\\ p=p''}}$$

$$+ \ldots, \qquad (2.8)$$

and substituting into the right hand side of (2.7) gives,

$$\int g(r,p,t;r',p',t)\,\phi(r,p)\,dr\,dp = \int g(r'',p'',t'';r',p',t')\,\phi(r'',p'')\,dr''dp''$$

$$+ \int g(r'',p'',t'';r',p',t')\Bigg\{\frac{\partial\phi}{\partial r''}\left[A_r(r'',p'')\Delta t + O((\Delta t)^2)\right]$$

$$+ \frac{\partial\phi}{\partial p''}\left[A_p(r'',p'')\Delta t + O((\Delta t)^2)\right] + \frac{\partial^2\phi}{\partial r''\partial p''}\left[B_{rp}(r'',p'')\Delta t + O((\Delta t)^2)\right]$$

$$+ \frac{1}{2}\frac{\partial^2\phi}{\partial r''^2}\left[B_{rr}(r'',p'')\Delta t + O((\Delta t)^2)\right] + \frac{1}{2}\frac{\partial^2\phi}{\partial p''^2}\left[B_{pp}(r'',p'')\Delta t + O((\Delta t)^2)\right]$$

$$+ O((\Delta t)^2)\Bigg\}\,dr''\,dp''\ . \qquad (2.9)$$

We integrate by parts, rearrange indices, and divide by Δt to obtain

$$\frac{1}{\Delta t}\int \phi(r,p)\,[g(r,p,t+\Delta t;r',p',t') - g(r,p,t;r',p',t')]\,dr\,dp$$

$$= \int \phi(r,p)\Big\{-\frac{\partial}{\partial r}[A_r(r,p)\,g(r,p,t;r',p',t')] -$$

$$-\frac{\partial}{\partial p}[A_p(r,p)\,g(r,p,t;r',p',t')] + \frac{\partial^2}{\partial r\partial p}[B_{rp}(r,p)\,g(r,p,t;r',p',t')]$$

$$+\frac{\partial^2}{2\partial r^2}[B_{rr}(r,p)\,g(r,p,t;r',p',t')] + \frac{1}{2}\frac{\partial}{\partial p^2}[B_{pp}(r,p)\,g(r,p,t;r',p',t')]$$

$$+ O(\Delta t)\Big\}\,dr\,dp \quad . \tag{2.10}$$

Multiplying both sides by $n(r',p',t')$, integrating over r' and p', and finally letting $\Delta t \to 0$ results in

$$\int \phi(r,p)\,[\frac{\partial n(r,p,t)}{\partial t}]\,dr\,dp = \int \phi(r,p)\Big\{-\frac{\partial}{\partial r}[A_r(r,p)\,n(r,p,t)] -$$

$$-\frac{\partial}{\partial p}[A_p(r,p,t)\,n(r,p,t)] + \frac{1}{2}[\ldots]\Big\}\,dr\,dp \tag{2.11}$$

and so, since the test function is arbitrary

$$\frac{\partial n}{\partial t} = -\frac{\partial}{\partial r}[A_r n] - \frac{\partial}{\partial p}[A_p n] + \frac{1}{2}\Big\{\frac{\partial^2}{\partial r^2}[B_{rr} n] + \frac{2\partial^2}{\partial r\partial p}[B_{rp} n]$$

$$+ \frac{\partial^2}{\partial p^2}[B_{pp} n]\Big\}. \tag{2.12}$$

The jump moments are calculated from the equations of motion. Integrating $p = m\dot{r}$ gives

$$m(r-r'') = m\int_t^{t+\Delta t} \dot{r}\,dt' = \int_t^{t+\Delta t} p(t')\,dt', \tag{2.13}$$

and so

$$\langle r-r''\rangle = \frac{1}{m}\int_t^{t+\Delta t} \langle p(t')\rangle dt' \approx \frac{p}{m}\Delta t\ , \tag{2.14}$$

which gives

$$A_r(r'',p'') \sim \frac{p}{m} \quad . \tag{2.15}$$

To obtain $\langle(r-r'')^2\rangle$ we square (2.13)

$$\langle(r-r'')^2\rangle = \frac{1}{m^2}\left\langle \int_t^{t+\Delta t} \int_{t'}^{t'+\Delta t} p(s)\,p(s')\,ds\,ds' \right\rangle$$

$$= \frac{1}{m^2}\langle(p\Delta t)(p\Delta t)\rangle$$

$$= \frac{p^2}{m^2}(\Delta t)^2$$

$$= O((\Delta t)^2) \quad .$$

$$\therefore \quad B_{rr}(r'',p'') \approx 0 \quad . \tag{2.16}$$

Similarly we may integrate (2.6a) and calculate the jump moments involving p, although it is necessary to use (2.2) and the fact that $\mathcal{F}(t)$ is random, i.e., $\int_t^{t+\Delta t} \mathcal{F}(t')dt' = 0$.

Substituting these moments into (2.12) finally gives the Kramers equation,

$$\frac{\partial n}{\partial t} = + \frac{\partial V(r)}{\partial r}\frac{\partial n}{\partial p} - \frac{p}{m}\frac{\partial n}{\partial r} + \eta\frac{\partial}{\partial p}\left[pn + mk_B T\frac{\partial n}{\partial p}\right] , \tag{2.17}$$

where $n \equiv n(r,p,t)$.

We next want to use the Kramers equation to study physisorption kinetics. Because a gas particle physisorbed onto a solid surface is rather weakly coupled to the thermal excitations of the solid, it will perform many oscillations in the surface potential well before it acquires enough

energy to desorb. This implies that the friction coefficient η in (2.17) is small, i.e. according to Suhl et al[20] that

$$\eta \ll \omega_o \frac{k_B T}{U_o} \quad , \tag{2.18}$$

where

$$\omega_o = \gamma \sqrt{\frac{2\,U_o}{m}} \tag{2.19}$$

is the angular frequency of oscillation at the bottom of the well of depth U_o and of range γ^{-1}. In the low friction limit the particle orbits in phase space, for many successive oscillations, are within the thermal fluctuations in r and p and can therefore be assumed closed for all practical purposes. This allows us to introduce, in a meaningful way, action and angle variables:

$$J = \oint p\,dr \quad , \tag{2.20}$$

$$w = \nu t = \frac{dE}{dJ}\,t \ . \tag{2.21}$$

Mathematically speaking, Kramers' equation cannot be written in terms of the action and angle without specifying the potential. However, Kramers has argued that by averaging (2.17) over an orbit in phase space it may formally be written as

$$\frac{\partial \bar{n}}{\partial t} = \eta \frac{\partial}{\partial J} \left[J\,\bar{n} + mk_B T \frac{J}{\nu} \frac{\partial \bar{n}}{\partial J}\right] \ , \tag{2.22}$$

where

$$\bar{n}(J,t) = \oint n(J,w,t)\,dw \ . \tag{2.23}$$

Let us emphasize that (2.23) is only a formal relation.

To study (2.22) further, in the context of physisorption kinetics, we need the relation between the action variable J and the frequency ν. It thus seems worthwhile to connect the action variable J to the energy E of the particle trapped in the surface potential. This can only be done after a potential V(r) has been specified.

Bak and Andersen[15] choose a potential $V(r) = C|r|^n$ and show that $E \propto J\nu$. Eliminating the action in favour of the energy in (2.22) and choosing boundary conditions appropriate for desorption, as well as an ansatz $\bar{n}(E,t) = n(E)\exp(-\lambda t)$, they have shown that n(E) can be expressed in terms of confluent hypergeometric functions and that λ^{-1} can be identified as the desorption time. We will present such an analysis in chapter III for the more realistic Morse potential,

$$V(r) = U_o(e^{-2\gamma(r-r_o)} - 2e^{-\gamma(r-r_o)}) , \qquad (2.24)$$

after we have derived (2.22) from the quantum statistical theory.

Recently, Caroli et al[12] have derived the Kramers-Langevin equation (2.1) starting from a microscopic model based on classical mechanics. This theory yields, for a Morse potential, a microscopic expression for the friction coefficient; namely

$$\eta \sim 4\omega_D \frac{m}{M_s} \left(\frac{u_o}{r}\right)^2 , \qquad (2.25)$$

where $u_o = U_o/\hbar\omega_D$, $r = 2m\omega_D/\hbar\gamma^2$, ω_D is the Debye frequency of the solid, and M_s is the mass of a solid atom.

II. 2 Quantum Statistical Theory

We will now outline the quantum statistical theory of physisorption as developed by Kreuzer et al[8,9,10]. According to quantum mechanics the surface potential will develop a number of bound states at energies E_i which may be occupied by an adsorbed gas particle. The probability of the gas particle being in energy state E_i is given by the occupation function n_i. It is assumed that the phonon-mediated transitions between different bound states as well as to and from the gas particle continuum may be regarded as a Markovian process and hence the occupation functions n_i are, at low coverage, subject to a set of rate equations,

$$\frac{dn_i}{dt} = \sum_{j\neq i} R_{ij}\, n_j - \sum_{j\neq i} R_{ji}\, n_i \quad , \tag{2.26}$$

where the indices i and j run over all bound states and continuum states accessible to the gas particle. The transition probabilities R_{ij} have been calculated by Gortel, Kreuzer and Teshima[8] for a one dimensional Morse potential (2.24) using second order perturbation theory.

For gas-solid systems such as Xe-W there are over a hundred bound states. It therefore seems reasonable to replace the sums over i and j by integrals over the scaled energy

$$\varepsilon = E/\hbar\omega_D \, . \tag{2.27}$$

Letting the occupation function go over into a function of energy,

$$n_i(t) \rightarrow n(\varepsilon_i, t) \; , \tag{2.28}$$

we may now write (2.26) as a continuous master equation[9],

$$\frac{\partial n(\varepsilon,t)}{\partial t} = \int_{-u_o}^{\infty} d\varepsilon' \rho(\varepsilon') W(\varepsilon,\varepsilon') n(\varepsilon',t) - \int_{-u_o}^{\infty} d\varepsilon' \rho(\varepsilon') W(\varepsilon',\varepsilon) n(\varepsilon,t) \, , \tag{2.29}$$

where

$$\rho(\varepsilon) = \frac{1}{\sqrt{|\varepsilon|}} \quad . \tag{2.30}$$

For the bound state-bound state transitions, i.e. for $-u_o < \varepsilon, \varepsilon' < 0$, Kreuzer et al[9] give the integration kernel as

$$W(\varepsilon,\varepsilon') = 3\pi\sqrt{r}\,\omega_D \frac{m}{M_s}\sqrt{\varepsilon\varepsilon'}\,(\varepsilon-\varepsilon')^3\,[\exp[\delta(\varepsilon-\varepsilon')]]^{-1}$$

$$\times \left\{ \theta(1-\varepsilon+\varepsilon')\,\theta(\varepsilon-\varepsilon')\, \frac{\Gamma(\sqrt{ru_o} - \sqrt{-r\varepsilon_o} + \frac{1}{2})\,\Gamma(\sqrt{ru_o} + \sqrt{-r\varepsilon} + \frac{1}{2})}{\Gamma(\sqrt{ru_o} - \sqrt{-r\varepsilon'} + \frac{1}{2})\,\Gamma(\sqrt{ru_o} + \sqrt{-r\varepsilon} + \frac{1}{2})} \right.$$

$$\left. + \theta(1-\varepsilon'+\varepsilon)\,\theta(\varepsilon'-\varepsilon)\, \frac{\Gamma(\sqrt{ru_o} - \sqrt{-r\varepsilon'} + \frac{1}{2})\,\Gamma(\sqrt{ru_o} + \sqrt{-r\varepsilon'} + \frac{1}{2})}{\Gamma(\sqrt{ru_o} - \sqrt{-r\varepsilon} + \frac{1}{2})\,\Gamma(\sqrt{ru_o} + \sqrt{-r\varepsilon} + \frac{1}{2})} \right\} \tag{2.31}$$

where θ is the step function and $\delta = \hbar\omega_D/k_BT$.

They also give the integration kernel for bound state-continuum transitions, i.e. for $-u_o < \varepsilon' < 0$ and $0 < \varepsilon < \infty$

$$W(\varepsilon,\varepsilon') = \frac{3\pi}{2}\sqrt{r}\,\omega_D \frac{m}{M_s}\sqrt{-\varepsilon\varepsilon'}\;\theta(1+\varepsilon')\theta(1+\varepsilon'-\varepsilon)$$

$$\times\left(\exp[\delta(\varepsilon-\varepsilon')]-1\right)^{-1}(\varepsilon-\varepsilon')^3\,\frac{\sinh(2\pi\sqrt{r\varepsilon})}{\sinh^2[\pi\sqrt{r\varepsilon}]+\cos^2[\pi\sqrt{ru_o}]}$$

$$\times\frac{|\Gamma(\sqrt{ru_o}+i\sqrt{r\varepsilon}+\frac{1}{2})|^2}{\Gamma(\sqrt{ru_o}+\sqrt{-r\varepsilon'}+\frac{1}{2})\Gamma(\sqrt{ru_o}-\sqrt{-r\varepsilon'}+\frac{1}{2})}\,, \qquad (2.32)$$

and for continuum-bound state transitions

$$W(\varepsilon',\varepsilon) = \frac{3\pi}{2}\sqrt{r}\,\omega_D \frac{m}{M_s}\sqrt{-\varepsilon\varepsilon'}\;\theta(1+\varepsilon')\theta(1+\varepsilon'-\varepsilon)$$

$$\times\left\{\left(\exp[\delta(\varepsilon-\varepsilon')]-1\right)^{-1}+1\right\}(\varepsilon-\varepsilon')^3\,\frac{\sinh(2\pi\sqrt{r\varepsilon})}{\sinh^2(\pi\sqrt{r\varepsilon})+\cos^2(\pi\sqrt{ru_o})}$$

$$\times\frac{|\Gamma(\sqrt{ru_o}+i\sqrt{r\varepsilon}+\frac{1}{2})|^2}{\Gamma(\sqrt{ru_o}+\sqrt{-r\varepsilon'}+\frac{1}{2})\Gamma(\sqrt{ru_o}-\sqrt{-r\varepsilon'}+\frac{1}{2})}\,. \qquad (2.33)$$

The integration kernel $W(\varepsilon,\varepsilon')$ is plotted in figures 1 and 2. Examining these figures we see that the bound state-bound state transition rates are much larger than the bound state-continuum transitions for most energy values. Physically this means that an adparticle will undergo many bound state-bound state transitions before desorbing. This large separation in time scales leads us to believe that the adparticle is executing a random walk amongst the bound state energy levels. We suspect that a Fokker-Planck equation will describe the adparticle kinetics. We also note that near the top of the potential ($\varepsilon=0$) the bound state-bound state and bound state continuum transition rates are of the same order of magnitude. We do not expect a Fokker-Planck type equation

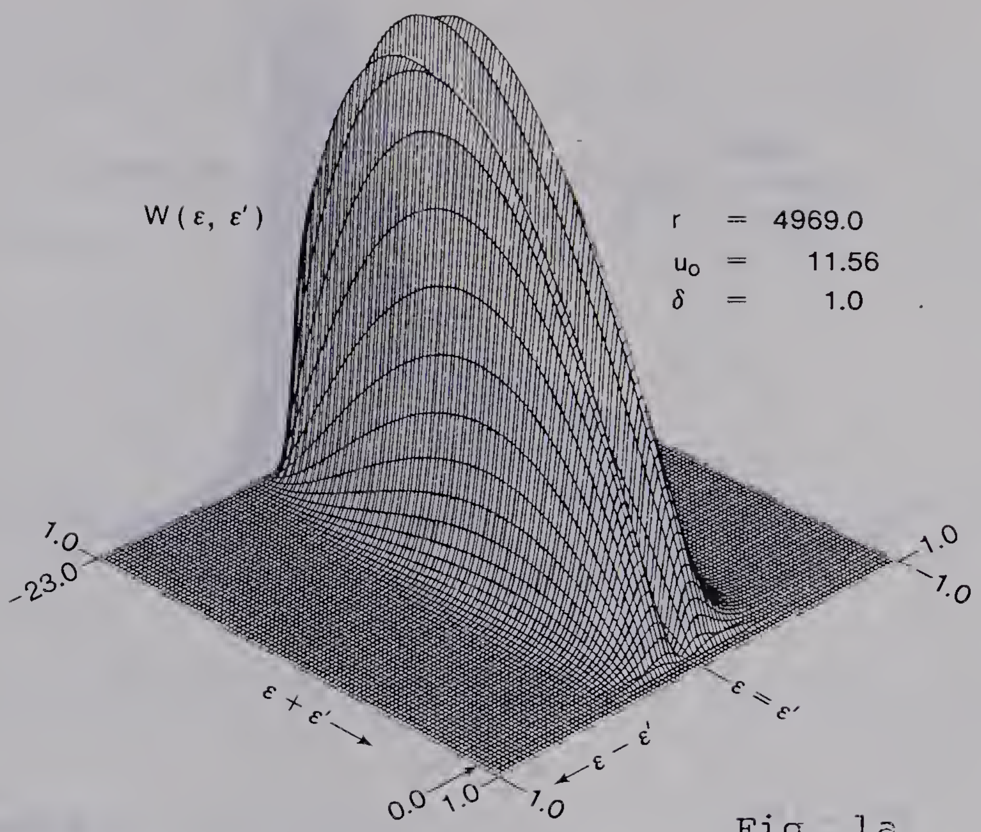


Fig. 1a

Fig. 1a and Fig. 1b.

The integration kernel $W(\varepsilon,\varepsilon')$ for the full range of ε and ε'. Courtesy of Prof. Kreuzer.

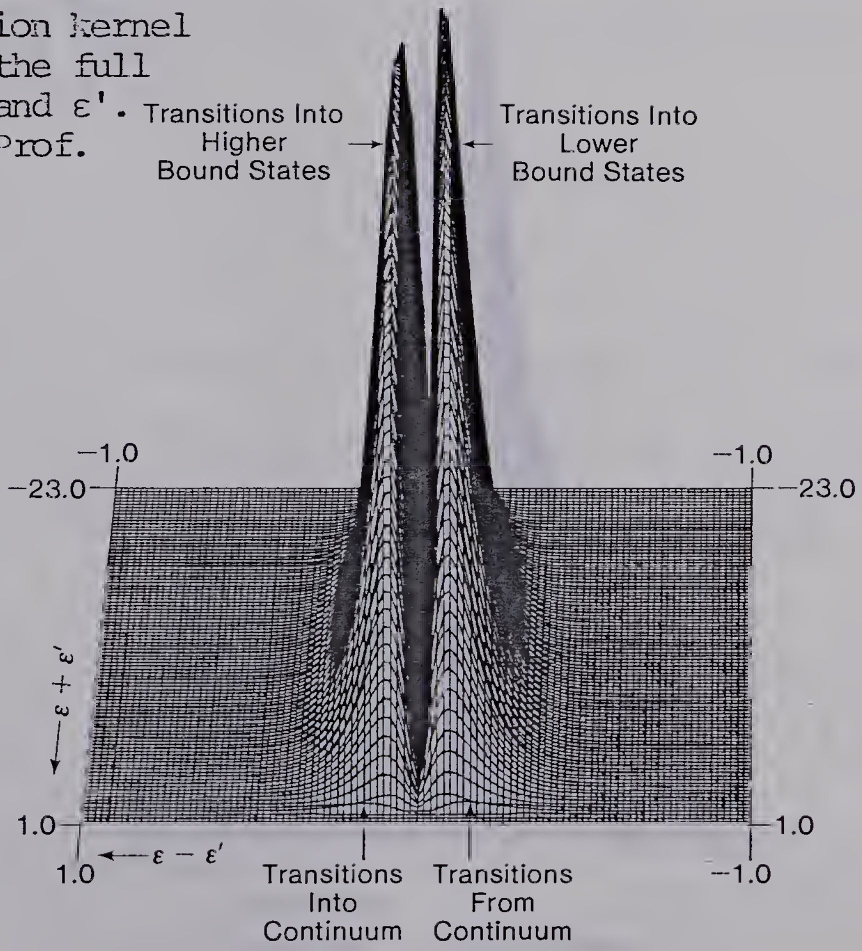


Fig. 1b

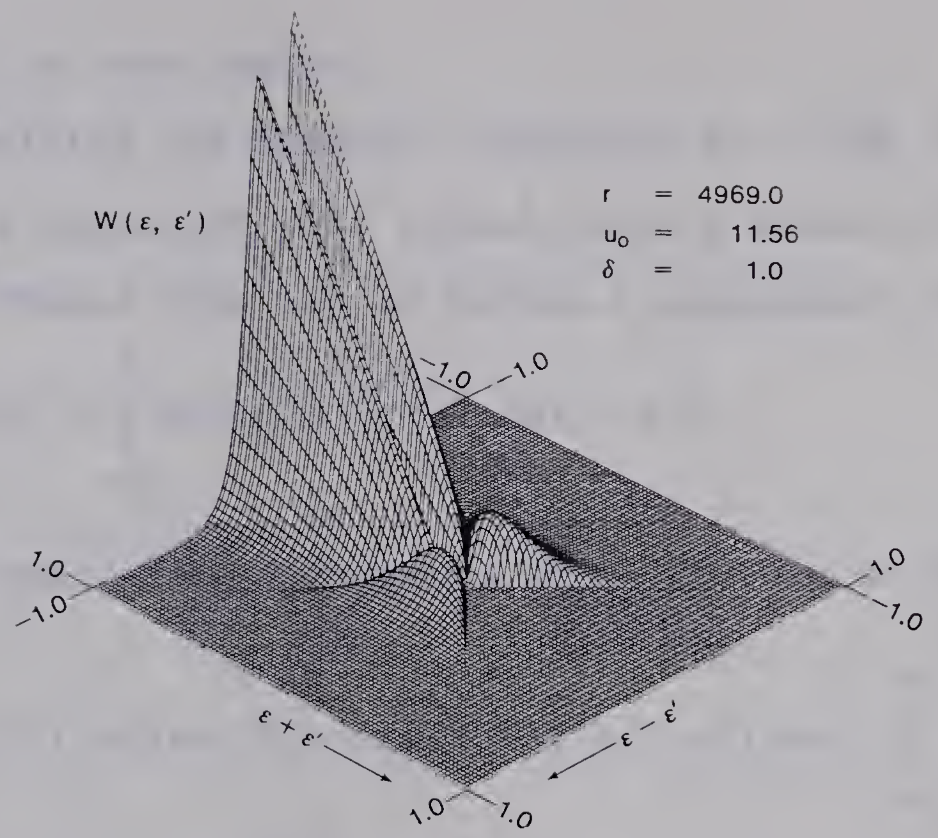


Fig. 2a

Fig. 2a and 2b.

The integration kernel at the top of the potential well shows a portion of fig. 1.

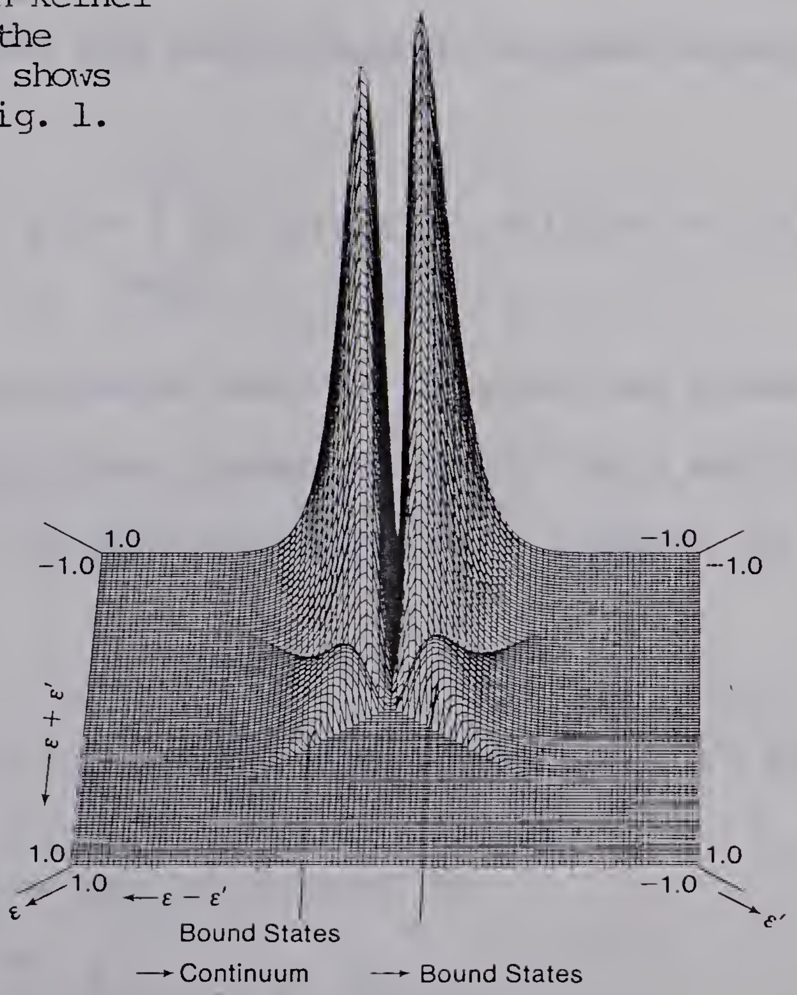


Fig. 2b

to be valid in this region.

Converting the integral operators in (2.28) into differential operators will indeed yield a Fokker-Planck equation. Toward this end we define a propagator $g(\varepsilon,t;\varepsilon't')$ by

$$n(\varepsilon,t) = \int_{-u_o}^{\infty} d\varepsilon'\, g(\varepsilon,t;\varepsilon',t')n(\varepsilon',t') \quad , \tag{2.34}$$

which, for small time increments $\Delta t = t-t'$, can be expanded as

$$g(\varepsilon,t+\Delta t;\varepsilon',t) = \delta(\varepsilon-\varepsilon') + \Delta t\Big\{\rho(\varepsilon)W(\varepsilon,\varepsilon') - \delta(\varepsilon-\varepsilon')\int_{-u_o}^{\infty} d\varepsilon'' \cdot \cdot\rho(\varepsilon'')W(\varepsilon'',\varepsilon')\Big\} \quad . \tag{2.35}$$

It also satisfies the Smoluchowski-Chapman-Kolmogorov equation

$$g(\varepsilon,t;\varepsilon',t') = \int_{-u_o}^{\infty} d\varepsilon''\, g(\varepsilon,t;\varepsilon'',t'')g(\varepsilon'',t'';\varepsilon',t') . \tag{2.36}$$

Following the procedure used to develop the Kramers equation, we multiply both sides of (2.36) by a well-behaved test function $\tau(\varepsilon)$ and integrate with respect to ε, to obtain,

$$\int_{-u_o}^{\infty}\tau(\varepsilon)\rho(\varepsilon)g(\varepsilon,t;\varepsilon',t')\,d\varepsilon = \iint_{-u_o}^{\infty} \rho(\varepsilon)\tau(\varepsilon)g(\varepsilon,t;\varepsilon'',t'')\, g(\varepsilon'',t'';\varepsilon',t')\cdot \cdot d\varepsilon\, d\varepsilon'' \tag{2.37}$$

The test function may be written as

$$\tau(\varepsilon) = \sum_{n=0}^{\infty} \frac{1}{n!}(\varepsilon-\varepsilon'')^n \tau^{(n)}(\varepsilon'') \quad , \tag{2.38}$$

which, upon substitution into the right hand side of (2.37) gives,

$$\int_{-u_o}^{\infty} \tau(\varepsilon)\rho(\varepsilon)g(\varepsilon,t;\varepsilon',t')d\varepsilon = \int_{-u_o}^{\infty} \tau(\varepsilon)\rho(\varepsilon)g(\varepsilon,t'';\varepsilon',t')\,d\varepsilon \; +$$

$$+ \Delta t \sum_{n=1}^{\infty} \frac{1}{n!} \int \tilde{\alpha}_n(\varepsilon'')g(\varepsilon,t;\varepsilon',t')\tau^{(n)}(\varepsilon'')d\varepsilon'', \qquad (2.39)$$

where, for small time intervals $\Delta t = t-t''$,

$$\tilde{\alpha}_n(\varepsilon'') = \frac{1}{\Delta t} \int_{-u_o}^{\infty} d\varepsilon\, \rho(\varepsilon)(\varepsilon-\varepsilon'')^n g(\varepsilon,t+\Delta t;\varepsilon'',t)$$

$$= \rho(\varepsilon'') \int_{-u_o}^{\infty} \rho(\varepsilon)(\varepsilon-\varepsilon'')^n\, W(\varepsilon,\varepsilon'')d\varepsilon = \rho(\varepsilon'')\alpha_n(\varepsilon'') . \qquad (2.40)$$

Rearranging terms and performing some necessary partial integration in (2.39) leaves us with,

$$\int \tau(\varepsilon)\rho(\varepsilon)\left(\frac{g(\varepsilon,t;\varepsilon',t') - g(\varepsilon,t-\Delta t;\varepsilon',t')}{\Delta t}\right) d\varepsilon$$

$$= \int \tau(\varepsilon)\rho(\varepsilon)\left\{\sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial \varepsilon^n}(\tilde{\alpha}_n(\varepsilon)g(\varepsilon,t;\varepsilon',t'))\right\} d\varepsilon \; . \qquad (2.41)$$

Taking the limit $\Delta t \to 0$ and multiplying (2.41) by $n(\varepsilon',t')$ and integrating over ε' gives, using (2.34),

$$\int \tau(\varepsilon)\left\{\frac{\partial}{\partial t}(\rho(\varepsilon)n(\varepsilon,t)) - \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial \varepsilon^n}(\tilde{\alpha}_n(\varepsilon)n(\varepsilon,t))\right\} d\varepsilon = 0 \; . \qquad (2.42)$$

Since (2.42) holds for any test function $\tau(\varepsilon)$, the expression in brackets is identically zero. Hence, (2.28) may be rewritten as a Kramers-Moyal expansion,

$$\frac{\partial}{\partial t}[\rho(\varepsilon)n(\varepsilon,t)] = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial \varepsilon^n}[\alpha_n(\varepsilon)\rho(\varepsilon)n(\varepsilon,t)] \; . \qquad (2.43)$$

Truncating the series at $n = 2$ gives a Fokker-Planck type equation,

$$\frac{\partial}{\partial t}\,[\rho(\varepsilon)n(\varepsilon,t)] = -\frac{\partial}{\partial\varepsilon}\,(\alpha_1(\varepsilon)\rho(\varepsilon)n(\varepsilon,t)) + \\ + \frac{1}{2}\,\frac{\partial^2}{\partial\varepsilon^2}\,(\alpha_2(\varepsilon)\rho(\varepsilon)n(\varepsilon,t)) \;. \tag{2.44}$$

We shall refer to this equation, with or without approximations to the moments $\alpha_1(\varepsilon)$ and $\alpha_2(\varepsilon)$, as the GKTT equation.

Kreuzer et al found approximate, analytic expressions for the moments α_1 and α_2, in the temperature regime,

$$\frac{5}{3}\,\frac{1}{u_o} << \delta << \sqrt{\frac{2}{5}\,\frac{r}{u_o}} \quad , \tag{2.45}$$

namely,

$$\alpha_1(\varepsilon) \approx +72\pi\,\omega_D\,\frac{m}{M_s}\,\sqrt{-r\varepsilon}\;A^{-5}\;[\frac{10B}{\delta A} - 1] \;, \tag{2.46}$$

$$\alpha_2(\varepsilon) \approx 6\pi\,\omega_D\,\frac{m}{M_s}\,\sqrt{-r\varepsilon}\;A^{-5}\;[\frac{24}{\delta} + \frac{120}{A^2} - \frac{2520B}{A^3}] \;, \tag{2.47}$$

where

$$A = \sqrt{\frac{r}{u_o}}\sqrt{\frac{u_o}{-\varepsilon}}\;\tanh^{-1}\sqrt{\frac{-\varepsilon}{u_o}} \quad , \tag{2.48a}$$

$$B = \frac{1}{4u_o}\sqrt{\frac{r}{u_o}}\;(-\frac{u_o}{\varepsilon})\left\{\frac{1}{1+\frac{\varepsilon}{u_o}} - \sqrt{\frac{u_o}{-\varepsilon}}\;\tanh^{-1}\sqrt{\frac{-\varepsilon}{u_o}}\right\} . \tag{2.48b}$$

Using these definitions and (2.44), Kreuzer et al were able to derive an approximate expression for the desorption time[10],

$$t_d \approx \frac{1}{72\pi}\,\omega_D^{-1}\,\frac{M_s}{m}\,\frac{r^2}{u_o^2}\,\frac{1}{\delta u_o}\,e^{\delta u_o} \quad , \tag{2.49}$$

and a macroscopic law[9],

$$\frac{\partial}{\partial t}\,\bar{\varepsilon} \approx \alpha_1(\bar{\varepsilon}) \tag{2.50}$$

where

$$\bar{\varepsilon} = \int_{-u_o}^{0} \varepsilon\, n(\varepsilon,t)\,\rho(\varepsilon)\; d\varepsilon \tag{2.51}$$

is the average energy of the adparticle.

III. THE GKTT EQUATION IN ACTION-ANGLE VARIABLES

III.1 Action-Angle Variables for a Morse Potential

The major task of this thesis is to relate the Kramers equation (2.22) used in the classical theories of desorption, to the GKTT equation (2.44), which was derived from a quantum mechanical theory of physisorption. To facilitate such a comparison we first introduce into (2.44) action and angle variables. We recall that this equation was derived for gas particles trapped in a one dimensional Morse potential (2.24), which we prefer now to write as

$$V(r) = U_o(e^{-\gamma(r-r_o)} - 1)^2 \tag{3.1}$$

by adding a constant U_o to (2.24). Starting from the Hamilton-Jacobi equation[16] for a gas particle of mass m in the potential (3.1)

$$\frac{1}{2m}\left(\frac{\partial W}{\partial r}\right)^2 + V(r) = E , \tag{3.2}$$

where $W = W(r,p)$ is Hamilton's characteristic function, we introduce in the standard way, the canonical momentum,

$$p = \frac{\partial W}{\partial r} \quad . \tag{3.3}$$

This may be inserted into the definition for the action variable (2.20) to obtain

$$J = \oint p\,dr = \oint \frac{\partial W}{\partial r}\,dr$$

$$= \sqrt{2mE} \oint \sqrt{1 - \frac{U_o}{E}\,(e^{-\gamma(r-r_o)} - 1)^2}\;dr \quad . \tag{3.4}$$

Setting $y = e^{-\gamma(r-r_o)}$ we get,

$$J = -\frac{\sqrt{2mE}}{\gamma} \oint \sqrt{-\frac{U_o}{E} + 2\frac{U_o}{E}\frac{1}{y} - (\frac{U_o}{E} - 1)\frac{1}{y^2}}\, dy$$

$$= \frac{2\pi}{\gamma}\sqrt{2m}\,[\sqrt{U_o} - \sqrt{U_o - E}\,] \quad . \qquad (3.5)$$

The action ranges in value from $J = 0$ at the bottom of the well $(E = 0)$ to

$$J = J_o = \frac{2\pi}{\gamma}\sqrt{2mU_o} \qquad (3.6)$$

at the top, where $E = U_o$. In dimensionless units we have

$$J_o = h\left(\frac{\sqrt{2mU_o}}{\hbar\gamma}\right) = h\sigma_o \quad . \qquad (3.7)$$

We may invert equation (3.5) to express E as a function of J

$$E = \frac{\gamma}{\pi}\sqrt{\frac{U_o}{2m}}\,J - (\frac{\gamma}{2\pi})^2\,\frac{J^2}{2m} \quad . \qquad (3.8)$$

A word of warning is in order here. The integral in (3.4) is not defined when $E = U_o$, i.e. when the particle is no longer confined to the surface region. It will be seen later that this introduces singularities into the Fokker-Planck (GKTT) equation. However, the singularity structure of the GKTT equation with suitably chosen expressions for the moments doesn't change.

We can now find the frequency of oscillation in the Morse potential by differentiating the energy with respect to the action,

$$\nu = \frac{dE}{dJ} = \frac{\gamma\sqrt{U_o}}{\pi\sqrt{2m}} - \left(\frac{\gamma}{2\pi}\right)^2 \frac{J}{m} \quad . \tag{3.9}$$

Using (3.8) the action J may be eliminated in favour of the energy E,

$$\nu = \frac{1}{2\pi}\sqrt{\frac{2\gamma^2}{m}\,(U_o - E)} \quad . \tag{3.10}$$

Note that this frequency is energy dependent as it must be for any realistic potential that develops both bound states and continuum states. At the bottom of the well the frequency is

$$\nu_o = \frac{\gamma}{\pi}\sqrt{\frac{U_o}{2m}} \quad . \tag{3.11}$$

We check this result by examining the small oscillations of the particle about the well minimum. Energy conservation gives us,

$$E = \frac{p^2}{2m} + V(r) = \frac{p^2}{2m} + U_o\left(e^{-\gamma(r-r_o)} - 1\right)^2 \quad . \tag{3.12}$$

For small displacements $(r-r_o)$ from r_o we may write the exponential term as

$$e^{-\gamma(r-r_o)} \approx 1 - \gamma(r-r_o) \ , \tag{3.13}$$

so that

$$E = \frac{p^2}{2m} + \frac{m}{2}\left(\sqrt{\frac{2U_o\gamma^2}{m}}\right)^2 (r-r_o)^2 \quad . \tag{3.14}$$

This is the energy of a particle executing harmonic motion with frequency

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{2U_o\gamma^2}{m}} = \frac{\gamma}{\pi}\sqrt{\frac{U_o}{2m}} \quad , \tag{3.11}$$

matching the result obtained for the Morse potential at $E = 0$. In closing this section let us note that the angle variable w, conjugate to the action J, is

$$w = \nu t + w_o = \frac{1}{2\pi}\sqrt{\frac{2\gamma^2}{m}(U_o - E)} + w_o \quad , \tag{3.15}$$

where w_o is a constant.

III.2 Transformation of the GKTT Equation to Action-Angle Variables

Before transforming the GKTT equation to action-angle variables we introduce a dimensionless action

$$x = \frac{J}{J_o} \quad , \tag{3.16}$$

where

$$J_o = \frac{2\pi}{\gamma}\sqrt{2mU_o} = h\sigma_o \tag{3.7}$$

is the action variable at the top of the Morse potential well. The frequency then is

$$\nu = \frac{\omega_D}{\pi}\frac{\sigma_o}{r}(1-x) = \frac{\omega_D}{\pi}\sqrt{\frac{u_o}{r}}\,(1-x) \quad , \tag{3.17}$$

and the energy is given by

$$\varepsilon = -\frac{\sigma_o^2}{r}(1-x)^2 = -u_o(1-x)^2 \quad . \tag{3.18}$$

For future reference we note that the Kramers equation (2.22) in terms of the variable x reads

$$\frac{\partial \bar{n}}{\partial t} = \eta \left\{ \frac{1}{2\delta u_o} \frac{\partial}{\partial x} \left[\frac{x}{1-x} \frac{\partial \bar{n}}{\partial x} \right] + \frac{\partial}{\partial x} [x\bar{n}] \right\} . \tag{3.19}$$

To transform the GKTT equation (2.44) we first differentiate equation (3.18) with respect to x and get

$$\frac{\partial \varepsilon}{\partial x} = 2u_o(1 - x) \quad , \tag{3.20}$$

so that the partial derivatives with respect to ε transform as

$$\frac{\partial f}{\partial \varepsilon} = \frac{\partial x}{\partial \varepsilon} \frac{\partial f}{\partial x} = \frac{1}{2u_o(1-x)} \frac{\partial f}{\partial x} \quad , \tag{3.21a}$$

and

$$\frac{\partial^n f}{\partial \varepsilon^n} = \left[\frac{\partial x}{\partial \varepsilon} \frac{\partial}{\partial x}\right]^n f$$

$$= \left[\frac{1}{2u_o} \frac{1}{1-x} \frac{\partial}{\partial x}\right]^n f$$

$$= \frac{1}{1-x} \left\{ \frac{(-1)^n}{(2u_o)^n} \sum_{k=1}^{n} (-2)^k \frac{(2n-1-k)!}{(k-1)!(n-k)!} \frac{\partial^k}{\partial x^k} \cdot \right.$$

$$\left. \cdot \left[\frac{f}{(1-x)^{2n-1-k}}\right] \right\} . \tag{3.21b}$$

Using (3.21a) the GKTT equation (2.44) reads, in the variable x,

$$\frac{\partial}{\partial t} [\rho(x)n(x,t)] = \frac{1}{8u_o^2} \frac{1}{1-x} \frac{\partial}{\partial x} \left\{ \frac{1}{1-x} \frac{\partial}{\partial x} [\alpha_2(x)\rho(x)n(x,t)] \right\}$$

$$- \frac{1}{2u_o} \frac{1}{1-x} \frac{\partial}{\partial x} [\alpha_1(x)\rho(x)n(x,t)] \quad , \tag{3.22a}$$

or since

$$\rho(x) = \frac{1}{\sqrt{u_o}\,(1-x)} \quad , \tag{3.23}$$

$$\frac{\partial n(x,t)}{\partial t} = \frac{1}{8u_o^2}\frac{\partial}{\partial x}\left\{\frac{1}{1-x}\frac{\partial}{\partial x}\left[\frac{\alpha_2(x)n(x,t)}{(1-x)}\right]\right\}$$

$$- \frac{1}{2u_o}\frac{\partial}{\partial x}\left[\frac{\alpha_1(x)n(x,t)}{(1-x)}\right] \quad . \tag{3.22b}$$

Alternatively, we may write (3.22) as,

$$\frac{\partial f}{\partial t} = \frac{1}{8u_o^2}\frac{\partial}{\partial x}\left[\frac{\alpha_2(x)}{(1-x)^2}\frac{\partial f}{\partial x}\right] - \frac{\partial}{\partial x}\left[\frac{\alpha_1(x)f}{2u_o(1-x)} + \frac{\alpha_2(x)-(1-x)\alpha_2'(x)}{8u_o^2(1-x)^3}f\right]$$

$$+ \left[\frac{\alpha_1(x)}{2u_o(1-x)} + \frac{3}{8u_o^2}\frac{\alpha_2(x)}{(1-x)^4}\right] f \quad , \tag{3.24}$$

where

$$f \equiv f(x,t) = \rho(x)n(x,t) \quad . \tag{3.25}$$

III.3 Some Comments on the Kramers-Moyal Expansion

The GKTT equation was derived[9] from the master equation (2.28) by a truncation of the Kramers-Moyal expansion (2.43) at $n = 2$. We want to examine briefly the question whether a Kramers-Moyal expansion in the variable x would after truncation also lead to equation (3.22). Using (3.21b) we get from (2.43),

$$\frac{\partial}{\partial t}[\rho(x)n(x,t)] = \sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\frac{1}{1-x}\left\{\frac{(-1)^n}{(2u_o)^n}\sum_{k=1}^{n}(-2)^k \cdot\right.$$

$$\left.\cdot \frac{(2n-1-k)!}{(k-1)!(n-k)!}\frac{\partial^k}{\partial x^k}\left[\frac{\alpha_n(x)\rho(x)n(x,t)}{(1-x)^{2n-1-k}}\right]\right\}. \tag{3.26}$$

Substituting (3.23) into (3.26), multiplying by (1-x) and interchanging the n and k summations gives

$$\frac{\partial n(x,t)}{\partial t} \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \frac{\partial^k}{\partial x^k} [\beta_k(x) n(x,t)] \ , \tag{3.27}$$

where

$$\beta_k(x) = k\, 2^k \sum_{n=k}^{\infty} \frac{(2n-1-k)!}{n!2^{2n}(n-k)!} \cdot \frac{1}{u_o{}^n} \frac{\alpha_n(x)}{(1-x)^{2n-k}} \quad . \tag{3.28}$$

This is a power series in $\frac{1}{u_o}$ which suggests that for $u_o >> 1$ a truncation at $n = 2$ is again possible, justifying equations (3.22) and (3.24). The condition $u_o >> 1$, or, $U_o >> \hbar\omega_D$, implies that the desorbing gas particles must undergo a great number of individual one-phonon absorption processes before it leaves the surface potential well.

Note also that the thermal fluctuations in the x variable, calculated with a Maxwell-Boltzmann distribution, are

$$\langle x^2 \rangle - \langle x \rangle^2 = \frac{1}{\delta u_o} = \frac{k_B T}{U_o} \quad . \tag{3.29}$$

With the inherent restriction $k_B T << \hbar\omega_D$, needed to justify the one-phonon calculation of the transition probabilities $W(\varepsilon,\varepsilon')$ (2.31), we see that the condition $u_o >> 1$ implies that the fluctuations should be small. This is important to keep in mind at the stage where we will try to approximate the moments $\alpha_n(x)$.

It is not known what relationship this expansion has to the method of expanding in a parameter Ω^{-1}, where

Ω is large, used by van Kampen[17,18] to justify the truncation of a Kramers-Moyal expansion.

III.4 Approximation of the Moments $\alpha_n(x)$

Approximate, analytic expressions for $\alpha_1(x)$ and $\alpha_2(x)$, in the limit of large r, have been obtained in ref. [9] and appear, respectively, as (2.46) and (2.47). In the x variable these equations read

$$\alpha_1(x) \approx +72\pi\, \omega_D \frac{m}{M_s} \frac{u_o^3}{r^2} (1-x)^6 [\tanh^{-1}(1-x)]^{-5} [\frac{10B}{\delta A} - 1], \qquad (3.30)$$

and

$$\alpha_2(x) \approx 6\pi\omega_D \frac{m}{M_s} \frac{u_o^3}{r^2} (1-x)^6 [\tanh^{-1}(1-x)]^{-5} [\frac{24}{\delta} + \frac{120\delta}{A^2} - \frac{2520B}{A^3}] , \qquad (3.31)$$

where

$$A = \sqrt{\frac{r}{u_o}} \frac{\tanh^{-1}(1-x)}{(1-x)} , \qquad (3.32)$$

and

$$B = \frac{1}{4u_o}\sqrt{\frac{r}{u_o}} \frac{1}{1-x} [\frac{1}{1-(1-x)^2} - \frac{\tanh^{-1}(1-x)}{(1-x)}] . \qquad (3.33)$$

To approximate $\alpha_1(x)$ and $\alpha_2(x)$, for intermediate values of x, by yet simpler expressions we resort to examining some numerical examples. From figures 3 and 4 we see that $\alpha_1(x)$ and $\alpha_2(x)$ are nearly quadratic in x away from $x=0$ and $x=1$. They are both off centre with a degree of asymmetry depending on δ; $\alpha_1(x)$ becomes more asymmetric for decreasing δ while the opposite is true for $\alpha_2(x)$. Both of the moments go to zero at $x=1$ and become very

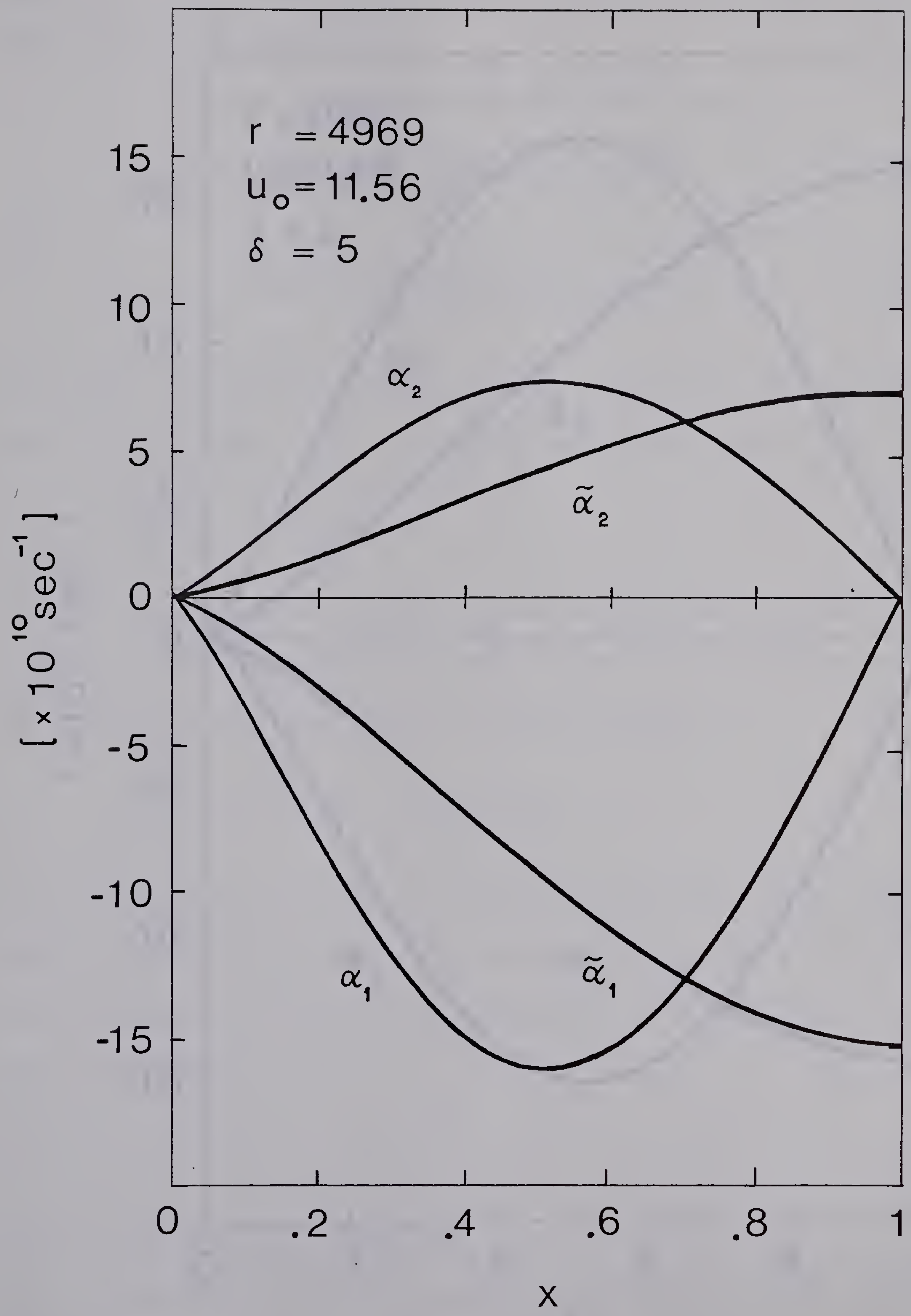
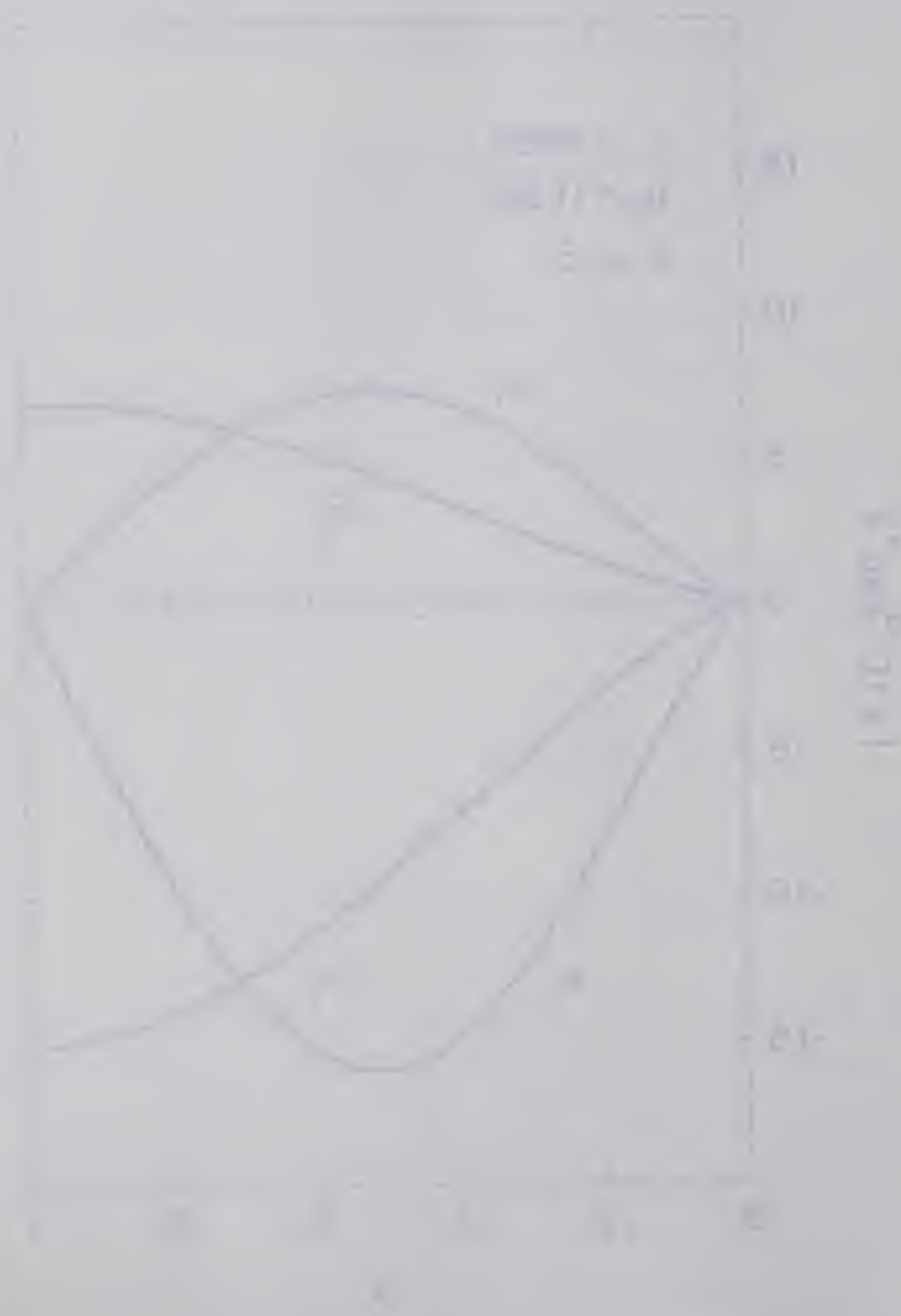

r = 4969
u$_o$ = 11.56
δ = 5
15
10
5
0
-5
-10
-15
[× 10^{10} sec^{-1}]
α_2
$\tilde{\alpha}_2$
α_1
$\tilde{\alpha}_1$
0
.2
.4
.6
.8
1
x

Fig. 3



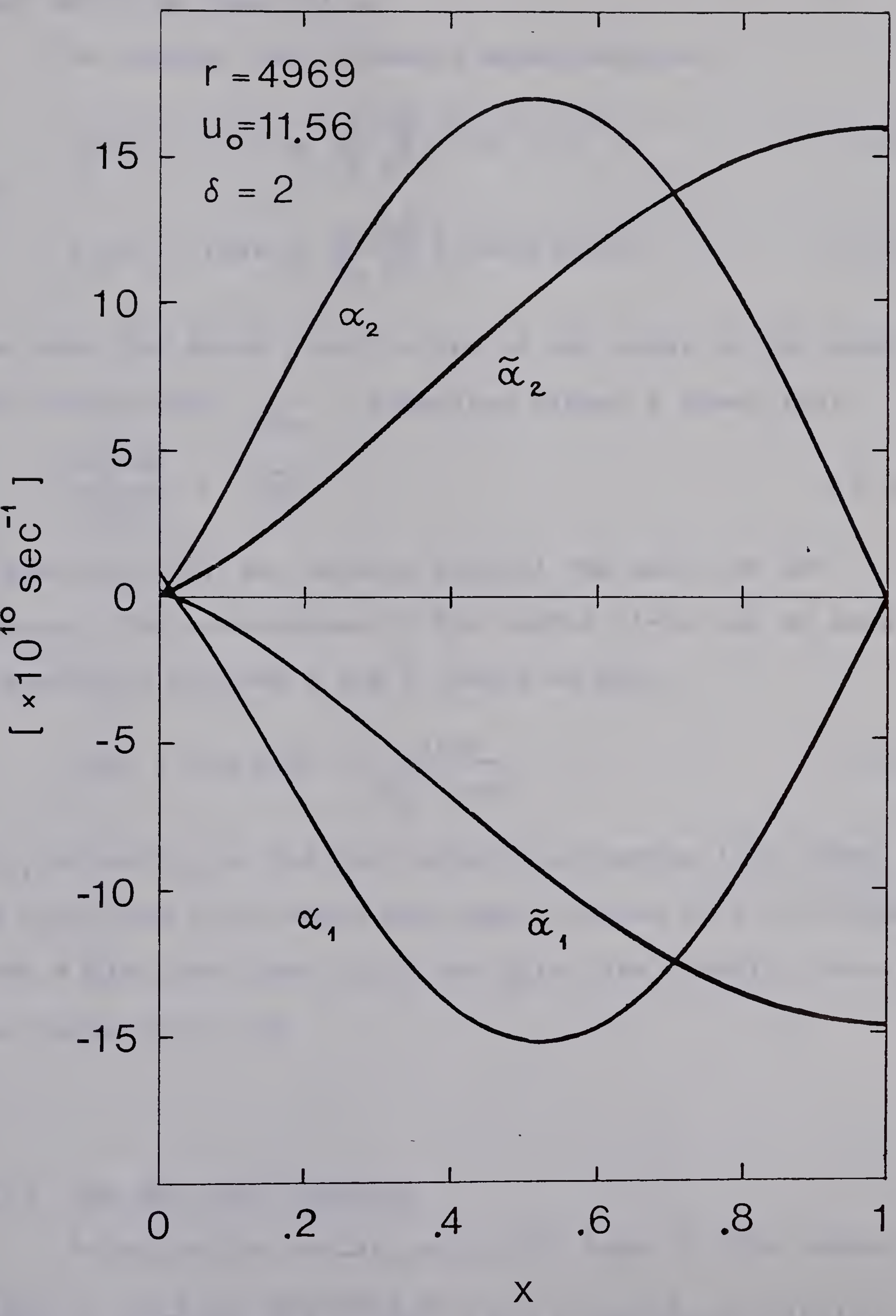


Fig. 4

small at $x = 0$. The moment $\alpha_1(x)$ crosses the x axis for a small positive value of x.

We propose the following approximation,

$$\alpha_1(x) \approx -72\pi\, \omega_D \frac{m}{M_s} \frac{u_o^3}{r^2} (x-a)(1-x) , \tag{3.34}$$

and

$$\alpha_2(x) \approx 144\pi\, \omega_D \frac{m}{M_s} \frac{u_o^3}{r^2} \frac{1}{\delta} (x+b)(1-x) . \tag{3.35}$$

Note that the zeros a and -b are of the order of the thermal fluctuations, $\frac{1}{\delta u_o}$. Examining figure 5 shows that

$$-\frac{2\alpha_1(x)}{\delta\alpha_2(x)} = \frac{x-a}{x+b} , \tag{3.36}$$

is qualitatively the correct form of the ratio of the moments. The correctness of the factor (1-x) can be seen by examining figures 3 and 4, where we plot

$$\tilde{\alpha}(x) = \alpha(x)\rho(x) = \frac{\alpha(x)}{\sqrt{u_o}\ (1-x)} . \tag{3.37}$$

If $\alpha_1(x)$ and $\alpha_2(x)$ did not contain the factor (1-x) then the $\tilde{\alpha}_1(x)$ and $\tilde{\alpha}_2(x)$ would not remain finite at $x = 1$. Figures 3 and 4 also show that $\tilde{\alpha}_1(x)$ and $\tilde{\alpha}_2(x)$ are roughly linear, with zeros near $x = 0$.

III.5 The New GKTT Equation

Substituting (3.34) and (3.35) into (3.22b) gives

$$\frac{\partial n(x,t)}{\partial t} = \eta \frac{\partial}{\partial x}\left\{ \frac{1}{2\delta u_o} \frac{x+b}{1-x} \frac{\partial n(x,t)}{\partial x} + (x - a + \frac{1}{2\delta u_o(1-x)}) n(x,t) \right\}, \tag{3.38}$$

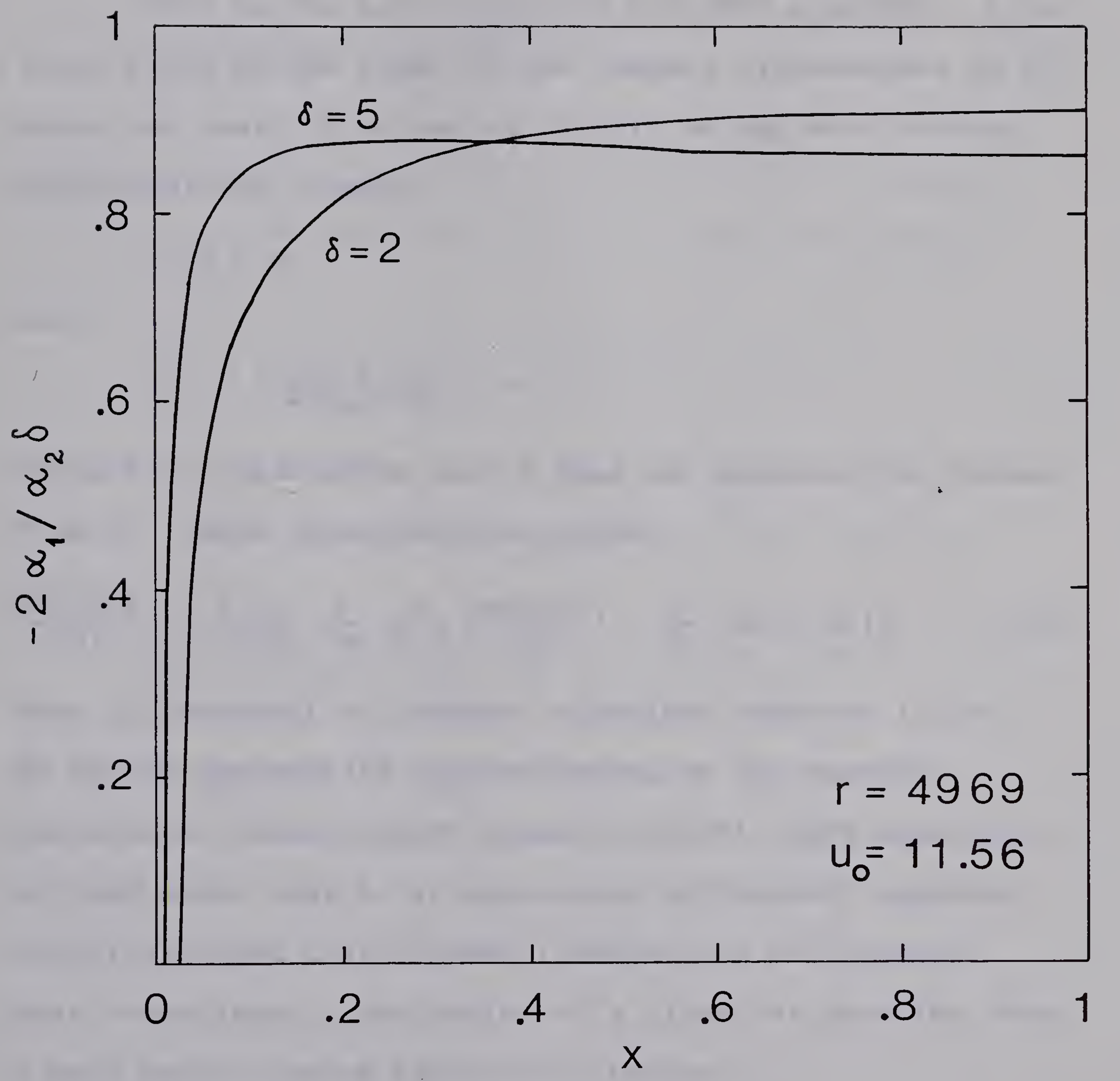


Fig. 5. A plot of the ratio $2\alpha_1(x)/\delta\alpha_2(x)$. The curve $y = \frac{x - .023}{x}$ ($a = 0.023$, $b = 0$) matches the curve for $\delta = 2$, to within a few percent. It is not shown since it lies on the curve for $\delta = 2$ most of the time

where

$$\eta = 36\pi\,\omega_D\,\frac{m}{M_s}\,\frac{u_o^2}{r^2}\ . \tag{3.39}$$

This is the new version of the GKTT equation. Since a and b are of the order of the thermal fluctuations in x, which are small by virtue of (2.45), we may make further approximations, namely

$$x + b \approx x\ ,$$

and

$$x - a + \frac{1}{2\delta u_o(1-x)} \approx x\ ,$$

where it is understood that x does not approach the values 0 or 1. These approximations yield,

$$\frac{\partial n(x,t)}{\partial t} = \eta\left\{\frac{1}{2\delta u_o}\,\frac{\partial}{\partial x}\left[\frac{x}{1-x}\,\frac{\partial n(x,t)}{\partial x}\right] + \frac{\partial}{\partial x}\left[x n(x,t)\right]\right\}. \tag{3.40}$$

This is identical to Kramers' classical equation (3.19). By making appropriate approximations to the quantum statistical Fokker-Planck equation (2.44) [GKTT equation], we have shown that it is equivalent to Kramers' equation (3.19) provided that thermal fluctuations are ignored. This constitutes a derivation of a classical equation from a more basic quantum statistical theory.

Now that the GKTT equation has been related to the Kramers' equation we may formally identify η as a friction coefficient. Before proceeding we wish to examine an alternate form of (3.40). Starting with

$$\frac{\partial f}{\partial t} = \frac{1}{8u_o^2}\frac{\partial}{\partial x}\left[\frac{\alpha_2(x)}{(1-x)^2}\frac{\partial f}{\partial x}\right] - \frac{\partial}{\partial x}\left[\frac{\alpha_2(x) f}{2u_o(1-x)} + \frac{\alpha_2(x)-(1-x)\alpha_2'(x)}{8u_o^2(1-x)^3}\right]$$

$$+ \left[\frac{\alpha_1(x)}{2u_o(1-x)^2} + \frac{3}{8u_o^2}\frac{\alpha_2(x)}{(1-x)^4}\right] f \;, \qquad (3.24)$$

where f is defined by (3.25), we substitute in equations (3.34) and (3.35) to obtain, after ignoring the thermal fluctuations,

$$\frac{\partial f}{\partial t} = \eta\left\{\frac{1}{2\delta u_o}\frac{\partial}{\partial x}\left[\frac{x}{1-x}\frac{\partial f}{\partial x}\right] + \frac{\partial}{\partial x}[xf] - \frac{x}{1-x} f\right\} . \qquad (3.41)$$

By using (3.7), (3.11), (3.13) and (3.14) we write equation (3.41) in terms of the action J and frequency of oscillation ν,

$$\frac{\partial f}{\partial t} = \eta\left\{\frac{\partial}{\partial J}\left[\frac{J}{\nu}k_B T\frac{\partial f}{\partial J}\right] + \frac{\partial}{\partial J}(Jf) - \frac{J}{J_o}\frac{\nu_o}{\nu} f\right\} . \qquad (3.42)$$

It is readily seen that (3.42) contains no quantities specific to the Morse potential and so should hold for any realistic surface potential appropriate for physisorption.

III.6 The Macroscopic Law of Friction and the Friction Coefficient

Kreuzer et al have obtained an approximate macroscopic law[9] from (2.44), namely,

$$\frac{\partial \bar{\varepsilon}}{\partial t} \approx \alpha_1(\bar{\varepsilon}) \quad , \tag{2.50}$$

where $\bar{\varepsilon}$ is the average scaled energy. This can be re-written, using (3.31), (3.15), and (3.26) as follows:

$$\text{L.H.S.} = \frac{\partial \bar{\varepsilon}}{\partial t} = \frac{\partial \bar{\varepsilon}}{\partial \bar{x}} \frac{\partial \bar{x}}{\partial t} = 2u_o(1-\bar{x}) \frac{\partial \bar{x}}{\partial t} \quad , \tag{3.43}$$

where

$$\text{R.H.S.} \approx \alpha_1(\bar{x}) = -72\pi\, \omega_D \frac{m}{M_s} \left(\frac{u_o}{r}\right)^2 u_o(1-\bar{x})(\bar{x}-a)$$

$$= -\, 2u_o \eta(1-\bar{x})(\bar{x}-a) \tag{3.44}$$

and so equating both sides and cancelling common factors gives us,

$$\frac{\partial \bar{x}}{\partial t} \approx -\, \eta(\bar{x}-a) \quad . \tag{3.45}$$

This is the macroscopic law of friction with friction coefficient η. The solution to equation (3.42) is

$$\bar{x} = a + (x_o - a)\, e^{-\eta t} \quad , \tag{3.46}$$

where x_o is the initial action of the particle. Physically this means that if a gas particle is put into a bound state $x = x_o$, it will lose or gain energy, exponentially, until its average value of x is $\bar{x} = a$, where a is of the order of a fluctuation from the bottom of the surface potential well.

This is the same interpretation put forward in ref. [9].

Note that the microscopic expression (3.39) for the friction coefficient,

$$\eta = 36\pi\,\omega_D \frac{m}{M_s} \frac{u_o^2}{r^2} = 9\pi \frac{U_o^2 \gamma^4}{m\,M_s \omega_D^3} \quad , \tag{3.39}$$

is, up to a constant the same as that obtained by Caroli et al in their microscopic model based on classical mechanics[12]. This agreement of quantum and classical theories seems to stem from the condition $u_o >> 1$ for the validity of the equations (3.22) and (3.24) which implies that a large number of one-phonon transitions are necessary to desorb a particle from the bottom of the surface potential well.

We can now calculate the friction coefficient η for a particular gas-solid system, which we choose to be Xe-W, to see if the low friction assumption is indeed satisfied. With the parameters[2] $\omega_D = 5.3 \times 10^{13}\ s^{-1}$, $\frac{m}{M_s} = .714$, $r = 4969$, and $u_o = 11.56$, we find $\eta = 2.3 \times 10^{10}\ s^{-1}$. To check whether this value is appropriate for the low friction limit we rewrite η in terms of the oscillation frequency at the bottom of potential, i.e. $\omega_o = \frac{\gamma}{\pi}\sqrt{\frac{U_o}{2m}}$, to get

$$\eta = 18\pi \frac{m}{M_s} \left(\frac{u_o}{r}\right)^{3/2} \delta u_o \left(\omega_o \frac{k_B T}{U_o}\right) \quad . \tag{3.47}$$

For Xe-W this implies $\eta \approx 0.1\left(\omega_o \frac{k_B T}{U_o}\right)$ and hence $\eta << \omega_o \frac{k_B T}{U_o}$ which is indeed Kramers' condition for low friction.

III.7 Desorption Kinetics

In this final section we shall study desorption kinetics based on

$$\frac{\partial n}{\partial t} = \eta \frac{\partial}{\partial x} \left\{ \frac{1}{2\delta u_o} \frac{x+b}{1-x} \frac{\partial n}{\partial x} + (x - a + \frac{1}{2\delta u_o (1-x)}) \, n \right\} . \qquad (3.38)$$

Before examining the time dependent solutions of (3.38) we first find its equilibrium solution. Setting $\frac{\partial n}{\partial t} = 0$ and ignoring terms of the order of the thermal fluctuations reduces (3.38) to

$$\frac{\partial}{\partial x} \left[\frac{1}{2\delta u_o} \frac{x}{1-x} \frac{\partial n}{\partial x} + xn \right] \approx 0 \; . \qquad (3.48)$$

The solution to (3.48) is

$$n(x) \approx c_1 \, e^{\delta u_o (1-x)^2} + c_2 \, e^{\delta u_o (1-x)^2} \int \frac{1-x}{x} \, e^{-\delta u_o (1-x)^2} \, dx \; , \qquad (3.49)$$

where the constants are determined by the boundary conditions. Setting $c_2 = 0$ gives

$$n(x) \approx c_1 \, e^{\delta u_o (1-x)^2} = c_1 \, e^{-\delta \varepsilon} \quad , \qquad (3.50)$$

which is a Maxwell-Boltzmann distribution in the energy. This justifies the use of the Maxwell-Boltzmann distribution to calculate the fluctuations in x (3.29).

To study the time-dependent solutions of (3.38) we assume that the variables can be separated and hence employ the ansatz[15,19]

$$n(x,t) = e^{-\lambda \eta t} \, g(x) \; , \qquad (3.51)$$

which, upon substitution into (3.38), gives

$$\frac{1}{2\delta u_o} \frac{\partial}{\partial x} [\frac{x+b}{1-x} \frac{\partial g}{\partial x}] + \frac{\partial}{\partial x} [x - a + \frac{1}{2\delta u_o} \frac{1}{1-x}] g + \lambda g = 0 \ . \quad (3.52)$$

Inserting

$$g(x) = (x+b)^{[2\delta u_o(b+a)(1+b)-1]} e^{-2\delta u_o(b+a)(x+b)} e^{\delta u_o(1-x)^2} h(x) \quad (3.53)$$

into (3.49) yields,

$$\frac{\partial}{\partial x}\left(\frac{(x+b)^{2\delta u_o(b+a)}}{2\delta u_o(1-x)} e^{-2\delta u_o(b+a)(x+b)} e^{\delta u_o(1-x)^2} \frac{\partial h(x)}{\partial x}\right)$$

$$+ \lambda e^{-2\delta u_o(b+a)(x+b)+\delta u_o(1-x)^2} (x+b)^{[2\delta u_o(b+a)(1+b)-1]} h(x)$$

$$= 0 \ . \quad (3.54)$$

This is the standard form of a Sturm-Liouville equation. Hence we may write the solution to (3.38) as

$$n(x,t) = e^{\delta u_o[(1-x)^2-2(b+a)(x+b)]} (x+b)^{[2\delta u_o(b+a)(1+b)-1]} \cdot$$

$$\cdot \left(\sum_{n=0}^{\infty} c_n e^{-\lambda_h \eta t} h_n(x)\right) \quad (3.55)$$

where λ_n and $h_n(x)$ satisfy equation (3.54) plus boundary conditions. For isothermal desorption the appropriate boundary conditions are,

$$n(x=1,t) = 0 \ , \quad (3.56)$$

and

$$\left(\frac{1}{1-x} \frac{\partial n(x,t)}{\partial x}\right)_{x=1} = 0 \ . \quad (3.57)$$

Unfortunately the eigenvalue problem defined by (3.54), (3.56) and (3.57) has yet to be solved. However, following Kreuzer and Teshima[10], we can find an approximate solution of (3.38), plus boundary conditions (3.56) and (3.57), by making an ansatz

$$n(x,t) = A\, e^{-t/t_d} \left(e^{\delta u_o (1-x)^2} - 1\right) , \tag{3.58}$$

which assumes a single desorption time, t_d, and an equilibrium x dependence. We also ignore terms of the order of the thermal fluctuations in (3.38) and get

$$\frac{\partial n}{\partial t} = \eta \frac{\partial}{\partial x} \left\{ \frac{1}{2\delta u_o} \frac{x}{1-x} \frac{\partial n}{\partial x} + xn \right\} \quad . \tag{3.40}$$

Substituting (3.58) into (3.40) and cancelling common factors gives,

$$t_d^{-1} \left(e^{\delta u_o (1-x)^2} - 1\right) = \eta \quad . \tag{3.59}$$

Now integrating both sides from zero to one yields, after rearranging terms,

$$t_d = \frac{1}{\eta} \left\{ \int_0^1 e^{\delta u_o (1-x)^2} dx - 1 \right\} \simeq \frac{e^{\delta u_o}}{2\eta \delta u_o} = \frac{1}{72\pi}\, \omega_D^{-1}\, \frac{M_s}{m}\, \frac{r^2}{\delta u_o^3}\, e^{\delta u_o} , \tag{3.60}$$

which was obtained by Kreuzer and Teshima. The dependence on η, which has already been obtained by Kramers[11], implies that the desorption process takes longer for smaller values of the friction. Smaller friction results, c.f. (3.39), when the range of the surface potential, $\frac{1}{\gamma}$, increases.

Although (3.60) was previously obtained in ref. [10], the above calculation did serve to justify some of the approximations made in the ansatz (3.58). In particular, the exponential term is appropriate because all terms in the general eigenfunction expansion (3.55) decay exponentially with time. For our analysis we also argued that the quasi-equilibrium assumption implies that terms of the order of the thermal fluctuations must be ignored.

An improved approximation for the desorption time might still be attainable though. Because equation (3.38) is of a relatively simple form we hope that keeping the thermal fluctuations may give a more accurate result for t_d. Alternatively, the lowest eigenvalue $\lambda_o \sim \frac{1}{t_d}$ might be obtained from perturbation theory.

IV. SUMMARY AND CONCLUSION

A detailed comparison of the low friction Kramers' equation, as derived from considerations based on classical mechanics, and the GKTT equation based on quantum statistical mechanics, has been made. This was achieved by casting both equations in terms of scaled action variables, and approximating the moments of the GKTT equation. It was found that if terms of the same order as the thermal fluctuations were ignored then the GKTT equation reduced to Kramers' equation. In contrast to the derivation of the Kramers-Langevin equation, by Caroli et al, from classical mechanics in the limit $m \gg M_s$, our derivation of Kramers' equation holds in the intermediate temperature regime, $\frac{5}{3u_o} \ll \delta \ll \sqrt{\frac{2r}{5u_o}}$, for weakly coupled gas-solid systems with a surface potential which develops a large number of bound states. An expression for the friction coefficient was also derived and was found to be identical, up to a multiplicative constant, to that derived by Caroli et al. This expression shows that the condition of weak coupling is indeed equivalent to low friction. The correspondence between classical and quantum theories we attribute to the large number of one-phonon events necessary for desorption to take place in weakly coupled gas-solid systems.

Some problems on the subject of Fokker-Planck equations for desorption remain. The derivation of the Fokker-Planck equation from a master equation has yet to

be entirely justified. In particular, the truncation of the Kramers-Moyal expansion for a system with finite boundaries has yet to be tied in with the formalism of van Kampen's large parameter expansion. It is also desirable to solve the eigenfunction and eigenvalue problem associated with the GKTT equation so that a more accurate expression of the desorption time may be found.

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